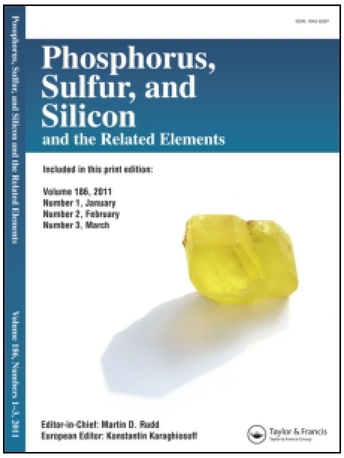

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Crystal Structure of the First Monomeric Organotellurium(IV) Oxide: Bis(2-dimethylaminomethylphenyl)tellurium(IV) Oxide

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The crystal structure of $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$ *was determined by X-ray diffraction on a single crystal. The crystal symmetry is monoclinic, space group* $P2_1$, *with unit cell dimensions* a $= 9.2274(2)$, b $= 10.1749(2)$, c $= 11.5339(3)$ Å, $\beta = 109.952°$, $V = 1017.90(4)$ Å^3 *and* $Z = 2$. *The structure has been solved and refined down to* $wR_2 = 0.0625$, *using 3675 independent reflections. The compound consists of isolated molecules with two intramolecular Te···N interactions of 2.565(4) and 2.755(6) Å stabilizing the tellurium atom.*

Keywords Crystal structure; donor-stabilization; tellurium

INTRODUCTION

Organotellurium compounds containing intramolecular Te···N interactions have been investigated over the past years.[1–16] In a recent report, we were able to provide clear evidence for the existence of the tellurenyl fluoride $2\text{-}Me_2NCH_2C_6H_4TeF$, with the help of the stabilizing 2-dimethylaminomethylphenyl ligand.[17] Besides other synthesized organotellurium(IV) compounds with this special nitrogen donor substituent, we also presented crystal structures of the organotellurium(IV) trifluoride $2\text{-}Me_2NCH_2C_6H_4TeF_3$,[17]

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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the organotellurium(VI) oxofluoride salt $[(2\text{-}Me_2NCH_2C_6H_4)_2TeF_3O]_2[SiF_6]$,[17] and the organotelluronium salt $[(2\text{-}Me_2NCH_2C_6H_4)_2TeOH]_2[SiF_6]$,[18] all characterized by intramolecular Te···N secondary interactions. To the best of our knowledge only a few examples for crystal structures of organotellurium(IV) oxides exist, among others Ph_2TeO, $(C_6F_5)_2TeO$ and $(p\text{-}MeOC_6H_4)_2TeO$.[19–28] However, all structures have in common that they exist as dimers, tetramers, or polymers with $[Te(\mu\text{-}O)]_n$ (n = 2, 4, ∞) units. In this article, we present a monomeric crystal structure of an organotellurium(IV) oxide.

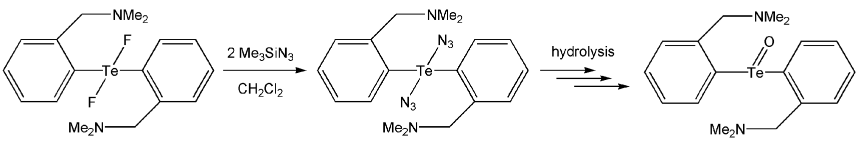
RESULTS AND DISCUSSION

The title compound $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$ was obtained as a hydrolysis product of the corresponding organotellurium(IV) diazide, which was prepared from the organotellurium(IV) difluoride with two equivalents of Me_3SiN_3 according to Scheme 1.[17]

The hydrolysis of the diazide, resulting from an incompletely closed vessel stored over a period of about 6 months, furnished the organotellurium(IV) oxide $(2Me_2NCH_2C_6H_4)_2TeO$. After a period of about 2 months, partially decomposition was already noticeable, which could be proven by ^{125}Te NMR spectroscopy. An additional resonance at $\delta = 1160$ ppm was found, which is shifted to lower field compared to the corresponding organotellurium(IV) diazide ($\delta = 1090$ ppm[17]) and was, after the structure elucidation, assigned to the title compound.

Suitable single crystals were obtained from a solution of $(2Me_2NCH_2C_6H_4)_2Te(N_3)_2$ in dichloromethane in a loosely closed vessel at ambient temperature. The compound crystallizes in the monoclinic crystal system, space group $P2_1$, with Z = 2 (see Figure 1).

The molecules exist as discrete monomers without significant intermolecular interactions below the sum of the tellurium–oxygen van der Waals radii (vdWr TeO 3.58 Å).[29] This is in contrast to known structures of organotellurium(IV) oxides, which were reported to exist as dimers (Ph_2TeO,[28] $(C_6F_5)_2TeO$,[22,23] and $OC(\mu\text{-}N^tBu)_2TeO$[24]) with two different Te–O distances, one characteristic double bond and an elongated coordinative bond, forming Te_2O_2 rings comprising bridging



SCHEME 1 Preparation of the tellurium(IV) diazide and the tellurium(IV) oxide as the product of hydrolysis.

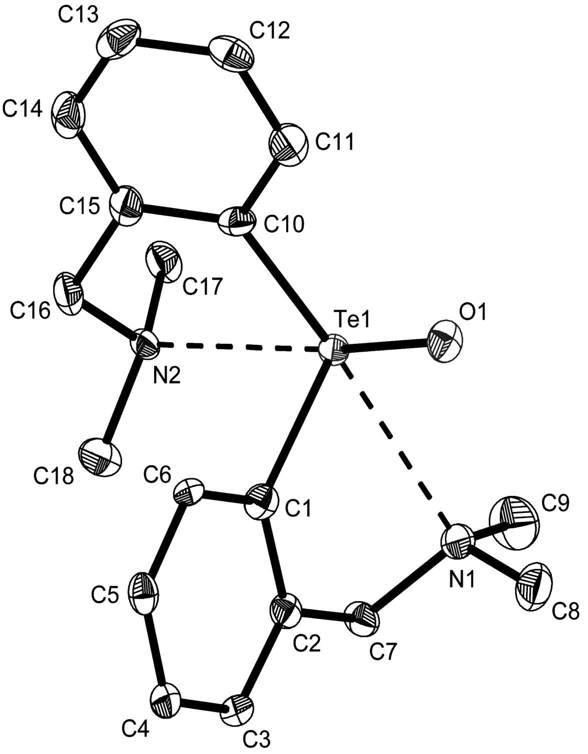


FIGURE 1 ORTEP plot of the crystal structure of $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$; H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Te1–O1 1.8293(10), Te1–C1 2.118(5), Te1–C10 2.134(5), Te1···N1 2.755(6), Te1···N2 2.566(5), C1–Te1–C10 97.7(2), C1–Te1–O1 92.60(18), C10–Te1–O1 89.69(19), O1–Te1···N1 82.40(13), O1–Te1···N2 159.66(17).

oxygen atoms. In case of $(p\text{-}MeOC_6H_4)_2TeO$, a polymeric $(TeO)_\infty$ chain with two slightly different Te–O distances is reported.[21] The Te–O distance in the title compound (1.829(1) Å) is slightly elongated compared to the calculated value of monomeric Ph_2TeO (1.814 Å),[30] but significantly shorter compared to the values for the tellurium oxygen double bonds in the crystal structures of Ph_2TeO (1.871(2) Å)[28] and $(C_6F_5)_2TeO$ (1.872(2)/1.87(1) Å).[22,23] Due to the bridging character of the oxygen atom in these compounds, the double bond character is reduced. This explains the elongated Te–O bonds compared to the bond distance in the title compound and also compared to the calculated monomeric Ph_2TeO. The same findings with an elongated Te–O bond distance with the 2-dimethylaminomethylphenyl substituent compared to the calculated value in the monomeric phenyl substituted compound Ph_2TeO were also reported previously for the hydroxytelluronium cation $[2\text{-}Me_2NCH_2C_6H_4TeOH]^+$ (calc.: 1.937 Å[30] vs. exp.: 1.961(2) Å).[18] Two intramolecular Te···N contacts of 2.755(6) Å (Te1···N1) and 2.565(4) Å (Te1···N2), slightly elongated compared to the contact distance in $2\text{-}Me_2NCH_2C_6H_4TeF_3$ (2.405(4) Å)[17] and considerably shorter compared to the distances in $(2\text{-}Me_2NCH_2C_6H_4)_2Te$ (3.048/3.145 Å),[8] are stabilizing the tellurium atom. These secondary interactions, significantly shorter than the sum of the tellurium–nitrogen van der Waals radii (vdWr TeN 3.61 Å[29]), are due to their sterical effects on the tellurium atom likely the reason for the monomeric structure. The Te–C bonds are in the range of common tellurium–carbon bond lengths (Te1–C1 2.117(5)/Te1–C10 2.135(5) Å vs. 2.099(4) Å in $2\text{-}Me_2NCH_2C_6H_4TeF_3$[17] and 2.12–2.20 Å in $(C_6F_5)_2TeO$[22,23]). The C1–Te1–C10 angle (97.78(18)°) is more bent compared to the values in the previously reported compounds (Ph_2TeO: 91.8(6)°[28] and $(C_6F_5)_2TeO$: 88.2(1)°/88.6(5)°[22,23]), which can also be explained as a result of the two secondary contacts of the coordinating substituent. This leads to a distorted octahedral arrangement around the tellurium atom, taking the free valence electron pair of the tellurium atom into account. The coordination of the aminomethyl nitrogen atoms creates two five-membered heterocycles with four-coordinated amine moieties.

A view of the unit cell along the *a*-axis of the title compound is shown in Figure 2. The packing can best be described as a layered structure along the 2_1 screw axes in the [010] direction.

EXPERIMENTAL SECTION

General Remarks

All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels.[31] The solvent dichloromethane was dried by standard methods stored under N_2 and freshly distilled prior to use. All reagents were used as received (Sigma-Aldrich, Fluka) if not stated otherwise. NMR spectra were recorded on a JEOL Eclipse 400 instrument at 25°C, and chemical shifts were determined with respect to Me_2Te (^{125}Te, 126.1 MHz).

X-Ray Crystallography

For the compound, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-K_α radiation

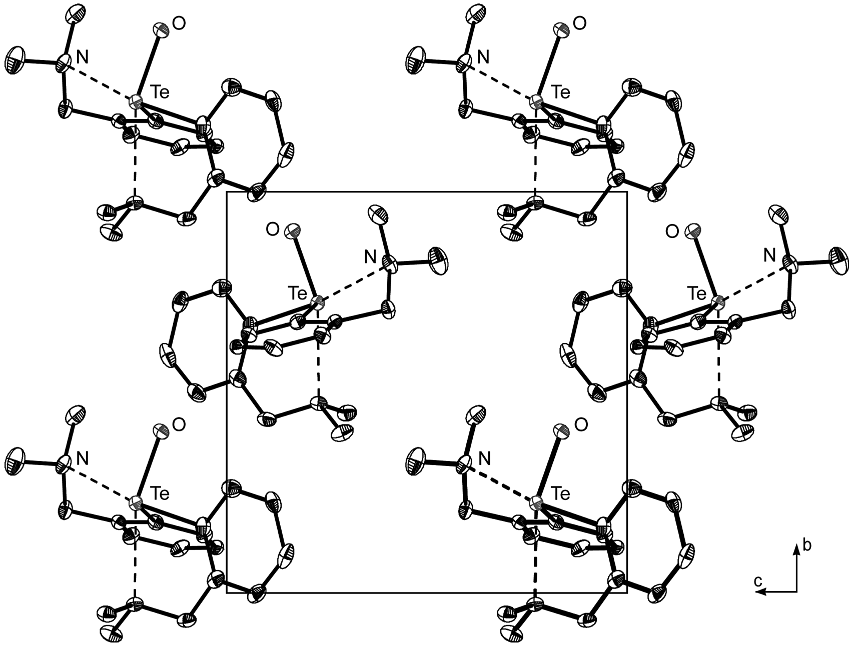


FIGURE 2 View of the unit cell of (2-$Me_2NCH_2C_6H_4$)$_2$TeO along [100]; H atoms omitted and only selected atoms labeled for clarity.

(λ = 0.71073 Å). The structure was solved using direct methods (SIR97[32]) and refined by full-matrix least-squares on F^2 (SHELXL[33]). All non-hydrogen atoms were refined anisotropically. Satisfactory atomic positions of the solvent molecules could not reliably be determined, therefore the disordered solvent was treated as a diffuse contribution using the program SQUEEZE.[34,35] SQUEEZE calculated 157 Å^3 void space per unit cell and 43 electrons; one molecule of dichloromethane requires 42 electrons per unit cell. The absolute structure was determined by refinement of the Flack parameter (Flack parameter = 0.04(3), 1585 Friedel pairs).[36,37] See Table I. ORTEP plots are shown with thermal ellipsoids at the 50% probability level. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre under the depository number CCDC-681994. Copies of the data can be obtained free of charge upon application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ; UK (Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

TABLE I Crystal and Structure Refinement Data

	$(2\text{-}Me_2NCH_2C_6H_4)_2TeO$
Empirical formula	$C_{18}H_{24}N_2O_1Te$
Formula mass	411.99
Temperature [K]	100
Crystal size [mm]	0.21 × 0.19 × 0.10
Crystal description	colorless block
Crystal system	monoclinic
Space group	$P2_1$
a [Å]	9.2274(2)
b [Å]	10.1749(2)
c [Å]	11.5339(3)
β [°]	109.952(3)
V [Å^3]	1778.0(2)
Z	2
ρ_{calc} [g cm^{-3}]	1.344
μ [mm^{-1}]	1.465
F(000)	412
θ range [°]	3.7–26.0
Index ranges	$-10 \leq h \leq 11$ $-12 \leq k \leq 12$ $-14 \leq l \leq 12$
Reflcns collected	5227
Reflcns observed	3205
Reflcns unique	3675 (R_{int} = 0.0245)
$R1$, $wR2$ (2σ data)	0.0273, 0.0615
$R1$, $wR2$ (all data)	0.0316, 0.0625
Max./min. transm.	0.851/0.754
Data/restr./param.	3675/0/203
GOOF on F^2	0.984
Larg. diff. peak/hole [e/Å^3]	0.307/–0.577

Formation of $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$

The reaction of $(2\text{-}Me_2NCH_2C_6H_4)_2TeF_2$ with two equivalents of Me_3SiN_3 furnished the tellurium(IV) diazide $(2\text{-}Me_2NCH_2C_6H_4)_2Te(N_3)_2$.[17] Single crystals of the tellurium oxide were obtained by storing a solution of the diazide in dichloromethane for 6 months in a loosely closed glass vessel at ambient temperature.

^{125}Te NMR ($CDCl_3$) δ 1160 ppm.

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